In-situ recovery of bio-butanol from glycerol fermentation using PDMS/ceramic composite membrane

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ABSTRACT

Pervaporation (PV) membranes have been attracted increasing attention in biofuels recovery owing to the higher separation efficiency and less harmful effect on microbes. Herein, we reported polydimethylsiloxane (PDMS) membrane coated on the inner surface of ceramic tube to in-situ recover bio-butanol from glycerol fermentation through PV process. The effects of butanol concentration, intermediates, raw material, inorganic salts and microbes on PV separation property of the PDMS/ceramic composite membranes were systematically discussed. After integrating with the membrane, bio-butanol was successively extracted from the fermentor, thereby remarkably reducing the butanol inhibition effect on microbial growth and thus greatly enhancing the yield and productivity of bio-butanol, from 0.35 to 0.40 g g$^{-1}$ and 0.09 to 0.17 g L$^{-1}$ h$^{-1}$, respectively. Meanwhile, the PDMS composite membrane presented an excellent separation property during the coupled process with 509 g/m$^2$ h for average total flux and 24.7 for butanol/water separation factor. In addition, the membrane fouling behavior was studied by characterizing the membrane microstructure and chemical property before and after using in the coupled process. Compared with the-state-of-the-arts, the PDMS composite membrane coupled with the process of glycerol fermentation presented here shows great potential in application of bio-butanol production.

1. Introduction

To date, the development and application of bio-butanol has a very important practical significance for alleviating the tense contradiction of the global oil supply and improving the worsening ecological environment [1–5]. Compared with bio-ethanol, bio-butanol has excellent properties in fuel performance and economy and gasoline compatibility (up to 20%) [6–8]. Like, ethanol, the traditional production method of bio-butanol also consumes agricultural products, so it is necessary to utilize multifarious organic waste for bio-butanol manufacture in order to solve the problem of grain fighting with people [9]. Therefore, the production of butanol with cheap and non-grain crops as feedstock is the direction of future development, such as liquefied corn starch, bagasse, corn straw, cassava and seaweed [10]. Generally, there are two challenges in the traditional fermentation process: the cost of feedstock and the inhibition of butanol [11,12]. To address the first challenge, the use of non-grain crops to replace traditional grain crops is an alternative choice.

In order to overcome the butanol inhibition on strains, it is commonly recognized coupling the bio-butanol fermentation process with separation for in-situ removal the fermentation product [13,14]. Compared with other separation processes, pervaporation membrane technology shows advantages in energy efficiency and less harmful effects on fermentation system [15–19]. Fermentation integrated with pervaporation process can not only alleviate the side effect of bio-butanol toxicity, but also improve the productivity and the utilization of feedstock [20–22].

Polydimethylsiloxane (PDMS), a representative alcohol-permeselective membrane with excellent separation performance and stability, has been widely applied for recovering bio-butanol from aqueous systems [23–27]. Wan et al. [28] investigated continuous ABE (acetone-butanol-ethanol) fermentation by combing silicalite-1 filled PDMS membrane. The experimental data confirmed that continuous recovery of ABE enhanced both the yield of products and the utilization rate of glucose. Qin et al. [17] studied ABE products recovery from fermentation solution with two pervaporation processes. After the second-
stage PV process in batch fermentation, 451.98 g L\(^{-1}\) of butanol was contained in the final product solution. Our previous work has realized PDMS membrane directly coupling with glucose fermentation where the membrane showed high flux of 670 g/m\(^2\) h and ABE solvent separation factor of 16.7 \[29\]. Previous literature has well demonstrated that pervaporation membrane for in-situ product removal from fermentor could slow down or eliminate the toxic effects of solvents on microbial growth. Therefore, the feedstock can be more effectively converted into product, thereby increasing yield and productivity of bio-butanol \[12\]. In addition, products of traditional fermentation to produce bio-butanol are butanol, acetone and ethanol with a volume ratio of 6:3:1 \[30\]. Namely, acetone and ethanol account for a half amount of the product, leading a low butanol titer and yield \[31, 32\]. In view of this issue, recently we reported an unparalleled Clostridium species strain CT7 and utilized glycerol as substrate to produce 10.0 g L\(^{-1}\) bio-butanol, meanwhile without acetone and very few ethanol (0.2 g L\(^{-1}\)) \[33\]. This new glycerol-based fermentation approach offer exciting opportunities for bio-butanol production \[6, 34\]. Therefore, it is meaningful that integration of membrane separation with this fermentation is expected to further enhance the fermentation production.

Due to the abundance of glycerol in biodiesel industry, we selected the glycerol as substrate to produce bio-butanol. With the lack of cfA/B gene in the whole genome, we successfully cultured acetone uncoupled Clostridium sp. strain CT7, which exhibited important advantages in the production of non-acetone and conduced to a high bio-butanol yield. PDMS membrane has extremely high selectivity to by-product acetone in ABE fermentation separation. Thus, in the BE fermentation, the PDMS membrane can concentrate more purity alcohol products than that of ABE fermentation. In this paper, therefore, we coupled PDMS/ceramic composite membrane with non-acetone fermentation for recovering bio-butanol from the BE fermentation to relief the solvent toxicity on microbial growth to improve the productivity. In comparison with our previous work, the separation layer (PDMS) was particularly coated on the inner surface rather than outer surface of ceramic tube, with the aim of having better flow distribution on membrane surface meanwhile avoiding physical damage during handling \[18\]. The effects of butanol concentration, glycerol, inorganic salts, and spent fermentation broth on the membrane property were studied. The properties of fermentation and membrane separation in the coupled process were systematically explored. Additionally, the membrane fouling in the actual fermentation coupled system was studied as well.

2. Experimental section

2.1. Preparation of PDMS/ceramic inner composite membrane

PDMS (hydroxyl terminated, Shanghai Synthetic Resin Company) polymer was mixed with n-heptane to form 10 wt% solution. Crosslinker tetraethylrhosilicate and catalyst dibutyltin dilaurate were gradually added into the solution with a mass ratio of \(W_{\text{polymers}} : W_{\text{crosslinker}} : W_{\text{cat}} = 100:10:1\). The resulting solution was reacted at 25 °C for 24 h and subsequently coated on inner surface of ceramic tube (ZrO\(_2\)/Al\(_2\)O\(_3\); 200 nm average pore size of inner surface; o.d.: 1.2 cm; i.d.: 0.8 cm). The as-prepared tubular composite membrane was dried at 25 °C for 24 h, and thermally treated at 120 °C for 12 h \[35\].

2.2. Culture and inoculum preparation

Soil samples (Laoshan Nature Park, Jiangsu, China) were obtained as inocula to sieve bacteria with bio-butanol production. The soil samples were mixed into anaerobic bottles, including 30 g L\(^{-1}\) of glycerol and 10 mL of defined mineral salts medium. After 48 h culture at 37 °C and 200 rpm/min, a little medium was spread on a Petri dish with RCA medium, and different colonies were added into mineral salts medium using glycerol for detection of their butanol capabilities. Finally, a unique bacterium (Clostridium species strain CT7) without acetone production was gained. In addition, Biomass growth was measured by optical density with a UV–visible spectrophotometer (LambdA, USA). Glycerol concentration was detected by an Agilent 1200 high-performance liquid chromatography as described in Jiang et al. \[33\]. Bio-products were analyzed by a 7890A gas chromatography (Agilent Technologies Inc.).

Fermentation solution was operated in a glass fermentor (5 L; Bioflo 110, America) with a 2-L effective working volume. When 200 mL secondary seed culture was inoculated, high-purity nitrogen was bubbled into the fermentation solution for 20 min to flash residual oxygen. The temperature of fermentation solution was adjusted to 37 °C and the stirred speed was maintained at 15 L h\(^{-1}\). Samples were checked timely and centrifuged at 10000 rpm for 2 min. Meanwhile, supernatants were applied for the analysis of bio-products by gas chromatography (GC-2014, Japan) fitted with Porapak Q column.

The bio-butanol fermentation solution was carried on in a 5-L bench-top fermentor employing the substrate of glycerol based on strain CT7 and included: KH\(_2\)PO\(_4\), 0.75 g L\(^{-1}\); K\(_2\)HPO\(_4\), 0.75 g L\(^{-1}\); CH\(_3\)COONa\(_2\)H\(_2\), 2 g L\(^{-1}\); yeast extract, 5 g L\(^{-1}\). Meanwhile, 1 mL of trace element solution (including FeCl\(_3\)), 1 mL of Na\(_2\)SeO\(_3\)-Na\(_2\)WO\(_4\) mixed solution and 0.01 g of resazurin were introduced to 1 L of the medium. After the medium was boiled and dropped to 25 °C under nitrogen protection, a certain mass of reductants (such as Na\(_2\)S, L-cysteine, and DL-dithiothreitol) were incorporated to the medium. Subsequently, 2-(N-Morpholino)ethanesulfonic acid was mixed into the medium to regulate the solution pH to 6.5. Finally, the medium was distributed to serum bottle, sealed with a butyl stopper, autoclaved for 20 min, and then lowered to 25 °C.

2.3. Pervaporation and PV-coupled fermentation experiment

The PV test was operated on a self-made device. The tubular composite membrane was sealed with silica O-rings and the effective membrane area was 89.49 cm\(^2\). The flow was adjusted to 15 L h\(^{-1}\) at 37 °C through the experimental process. Meanwhile, permeate side pressure of the membrane was less than 250 Pa. Cold traps were exchanged from time to time to collect the products continuously. The products were detected by gas chromatography (GC-2014, Japan) using the carrier gas of nitrogen. All the collections were repeated no less than 3 times to keep the error below 10%.

The evaluation of the membrane performance is mainly through the permeation flux \(J\) and separation factor \(\alpha\), which are obtained from Eqs. (1) and (2), respectively:

\[
J = \frac{m}{At}
\]  
\[\alpha = \frac{y_1/y_2}{x_1/x_2}
\]

where \(m\) is the weight of the permeate side product, \(A\) is the effective membrane area, and \(t\) is the permeation time; \(y\) and \(x\) are the weight percentages of each components in permeate and feed side, respectively.

The flux of each component \(i\) is obtained as:

\[
J_i = C_{\text{permeate}}J
\]

where \(C_{\text{permeate}}\) represents the content of each component \(i\) in the permeate side.

The separation factor gained through the PV processes for each component \(i\) to water are considered as:

\[
\alpha_i = \frac{y_i/(1 - y_i)}{x_i/(1 - x_i)}
\]
To monitor the fermentation and separation process, broth samples are analyzed timely for biomass growth, residual glycerol, ethanol, acetic acid, bio-butanol and butyric acid content. After appropriate dilution, biomass was adjudicated by evaluating optical density at the wavelength of 600 nm by UV–visible spectrophotometer (Lambda-25, America). Glycerol was tested at 75 °C with 0.6 mL/min eluent of 5 mM sulfuric acid by a high-performance liquid chromatography (Agilent Technologies Co.) supplied with a Refractive Index Detector. Bio-products and acids were analyzed by gas chromatography (Agilent Technologies Co.).

In the fermentation-pervaporation coupled experiment (Fig. 1), through the preferential selectivity of the pervaporation membrane, the volatile components in the fermentor are in-situ removed, while the nutrients, feedstock, and microbiological cells are rejected. Before the beginning of the experiment, the membrane module and pipelines that could touch the fermentation solution were disinfected for 15 min at 121 °C by a sterilization equipment. After butanol concentration is reached to 6.0 g L\(^{-1}\) in the fermentor, the sterile pervaporation system was coupled to conduct continuous fermentation and in-situ separation.

3. Results and discussion

3.1. Morphology of PDMS/ceramic composite membrane

Fig. 2 exhibits the cross-section and surface SEM images of PDMS coated inner surface of ceramic composite membrane. The thickness of PDMS layer is optimized at around 5 \(\mu\)m (Fig. 2a) to provide a thin and defect-free membrane layer. A suitable transition layer between the separation layer and the support layer is conductive to improve the interfacial bonding force. On the one hand, the increase of the transition layer thickness would increase the transport resistance and thus lower the membrane flux. On the other hand, an excessively thin film layer is prone to be defective and have insufficient interfacial adhesion [25]. The top surface of PDMS layer presents dense and defect-free (Fig. 2b).

3.2. Effect of individual components in fermentation solution on membrane performance

Butanol is the main product of the fermentation, thus the variation of separation property of the PDMS composite membrane with the content of \(n\)-butanol in water ranging from 0.5 to 2.5 wt% was studied. As shown in Fig. 3, along with the adding of \(n\)-butanol in the solution, the total flux was almost linearly increased while the separation factor was decreased. On account of the solution-diffusion model for PV
process, enhancing n-butanol content in the feed is beneficial to the n-butanol sorption in the polymeric layer, thereby swelling the PDMS chains to enhance the diffusion and increase the total flux. In addition, the enhanced driving force across the membrane and butanol sorption in the PDMS layer with higher butanol content in the feed can also enhance the total flux. Meanwhile, the diffusion of n-butanol is lower than that of water in virtue of the smaller molecular size, thus leading to a decline of separation factor of butanol over water.

Apart from butanol, the fermentation process also produces other solvents, including ethanol, acetic acid and butyrate acid, with a typical percentage of 0.04 wt%, 0.06 wt% and 0.57 wt%, respectively. The influence of these volatile solvents (refer to simulated fermentation products) on the PV property of butanol/water was thus explored. As shown in Fig. 4, compared with the binary butanol-water mixtures, the total flux was increased in the simulated fermentation products system, due to the permeation of these solvents through the PDMS membrane layer. As expected, the ethanol/water separation factor is ~6.0 that agrees well with the intrinsic property of PDMS membrane [36]. The separation factors for acetic acid and butyrate acid are almost equal to 1.0, indicating that the PDMS membrane nearly shows non-selective permeation for organic acids. This result is particularly favorable for the coupled process since these acids are the intermediate products for the final products (ethanol and butanol) and should not be removed by pervaporation from the broth during the fermentation.

We further added inorganic salts, whose contents followed the recipe used for the fermentation, into the simulated fermentation products system (Fig. 4). A higher separation factor was observed with addition of inorganic salts into the system, which is consistent with Lipnizki et al. [37] who investigated the role of different kinds of inorganic salts on the pervaporation performance of 1-propanol/water mixtures through PDMS membrane. This phenomenon, called salting-out effect, is mainly due to changes in activity coefficient with the existence of inorganic salts in the feed [38].

The role of substrate glycerol on the membrane property for n-butanol/water separation was also investigated. As shown in Fig. 5, compared to the n-butanol/water binary system, the addition of 6.5 wt % glycerol led to a slightly lower separation factor. Very low content of glycerol (< 0.1 wt%) was detected in the membrane permeate with a high rejection rate of > 98.5%. It indicates that glycerol, with a high boiling point of 290.0 °C, could hardly evaporate during the pervaporation process, which is highly desirable because the substrate of material glycerol should not be removed from the fermentation broth.

Before applying the PDMS membrane in the coupled process of glycerol fermentation-PV, we evaluated the membrane performance in a spent fermentation broth (i.e., a broth from a finished batch fermentation). As shown in the Fig. 5, the overall performance was decreased, especially for the separation factor. To a certain extent, in the spent fermentation solution, the inactive microbial cells and the incomplete consumption of glycerol reduced the membrane selectivity. Fortunately, after a simple water rinsing, the separation property the PDMS membrane can be generally recovered, implying that the negative effect of spent fermentation broth is reversible.
3.3. Fermentation and membrane performance in coupled process

Batch fermentation without or with integrating membrane separation process was operated to investigate the role of in-situ product separation by the PDMS/ceramic composite membrane. It should be noted that the membrane area used for above performance measurement in Section 3.2 is 32.66 cm², which was found to be insufficient to match the solvent removal rate for the fermentation process with total volume of 2L. Thus, we decided to scale up the tubular PDMS/ceramic composite membrane from effective length of 15 cm to 40 cm. By using the same coating procedure for the short ceramic tube (15 cm), lower flux is generally obtained due to a thicker PDMS layer formed at the bottom of the ceramic tube with larger length (40 cm). By further optimizing the polymer solution properties and coating process, currently we can scale up the PDMS/ceramic inner composite membrane with the length of 80 cm meanwhile achieving a good separation performance: total flux of 719 g/m² h and separation factor of 22.1 for butanol/water. Improvement of the scale-up process is still undergoing in our lab, which will be reported in our near future work.

Glycerol (60 g L⁻¹) was consumed for the butanol production with C. pasteurianum CT7 in broth cases. In the fermentation alone process (Fig. 6a), the products are accumulated in the broth, showing gradual increases of concentration during the fermentation, reaching butanol content of 10.62 g L⁻¹ and ethanol content of 0.42 g L⁻¹ in the final. Acetone and other substances were not detected except for 0.59 g L⁻¹ acetic acid and 5.72 g L⁻¹ n-butyric acid. Through the process of PV-coupled fermentation, the in-situ separation process was started after the fermentation time reached 48 h and the butanol content in the solution was up to 6 g L⁻¹. As shown in Fig. 6b, the continuous products removal by the pervaporation membrane led to a low product concentration (< 6 g L⁻¹) in the broth. Such low solvent concentration is beneficial to the growth of microorganisms because the inhibition of butanol is relieved, as evidenced by stabilized OD value in the PV-integrated fermentation process. Moreover, in contrast to the half utilization of glycerol in the fermentation alone process, the glycerol is fully utilized after coupling PV separation with the fermentor. Accordingly, the solvent productivity is significantly improved.

The overall fermentation performance is given in Table 1. Compared with fermentation alone, the integration of PV separation increased the yield and productivity of bio-butanol from 0.35 g g⁻¹ to 0.43 g L⁻¹ h⁻¹ in the coupling process, which is 72% higher than that in the fermentation alone. In the coupled process (Fig. 7), the PDMS composite membrane exhibits a stable separation factor for both butanol and ethanol, in which the fluctuation can be owing to the changes of product content in the fermentor. The total flux is decreased from an initial 570.9 g/m² h to a stable 480.8 g/m² h after fermentation for 70 h. According to the role of bio-butanol concentration on the membrane property presented in Fig. 3, the decrease of bio-butanol content in the fermentor (6 g L⁻¹ at 30 h to 1.0 g L⁻¹ at 115 h) might contribute to the flux decline. Meanwhile, the bio-fouling of membrane, originating from the attachment of microbes on the surface of PDMS membrane would also reduce the flux [29].

In order to understand the flux decline in the coupled process, we examined the microstructures and chemical properties of the PDMS membrane before and after the integration. The morphology of the used PDMS membrane is exhibited in Fig. 8. Some residual bacteria were surveyed on the membrane surface, indicating an occurrence of biofouling. While the bacteria coverage is significantly lower than that of the PDMS layer coated on the outer surface of ceramic tube in our previous work [29]. The detailed reason will be discussed later.

AFM images of the fresh and used membranes (Fig. 9) turn to be diverse significantly in the 5 × 5 μm² scanning area, especially in morphology and surface roughness. The surface of the fresh PDMS layer was ultra-smooth, while that of the used membrane was rough.

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**Table 1**

<table>
<thead>
<tr>
<th>Fermentation mode</th>
<th>Fermentation alone</th>
<th>PV-integrated fermentation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butanol yield (g g⁻¹)</td>
<td>0.35</td>
<td>0.40</td>
</tr>
<tr>
<td>Butanol productivity (g L⁻¹ h⁻¹)</td>
<td>0.09</td>
<td>0.17</td>
</tr>
<tr>
<td>Glycerol consumption (g L⁻¹)</td>
<td>29.7</td>
<td>51.4</td>
</tr>
<tr>
<td>Glycerol consumption rate (g L⁻¹ h⁻¹)</td>
<td>0.25</td>
<td>0.43</td>
</tr>
</tbody>
</table>

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*Fig. 6.* Variation of fermentation products and glycerol concentration in fermentation broth using C. pasteurianum CT7. (a) Fermentation alone; (b) PV-integrated fermentation.

*Fig. 7.* Pervaporation performances of PDMS composite membrane through the process of PV-coupled fermentation.
increased roughness in the used membrane surface would be ascribed to the adsorption of organic foulants by combining the result of SEM characterization (Fig. 8b).

Fig. 10 shows the FT-IR spectra of the fresh PDMS membrane, used membrane and C. pasteurianum CT7. Two strong absorption peaks of Si(CH$_3$)$_2$ at 865 and 785 cm$^{-1}$ were observed. The characteristic absorption peaks of Si–O bonds appear at 1093 and 1006 cm$^{-1}$, implying the existence of Si–O–Si bonds. This means that the polymerization between PDMS and tetraethylrthosilicate occurs with the aid of catalyst. The characteristic peaks at 2963, 2905 and 1261 cm$^{-1}$ are in accord with the asymmetric C–H stretch from –CH$_3$. These characteristic peaks further confirm the existence of crosslinking in the PDMS membrane. The spectrum has a broad region of absorption at 3450 cm$^{-1}$ because of the stretching of the O–H bond in hydroxyl groups [39]. It is a broad peak at 1200–1000 cm$^{-1}$, which is attributed to C–O bonds involved in alcohols and carbohydrates [40]. The explanation for this peak is usually ascribed to the appearance of biologic cell. Two sharp peaks (1632 and 1578 cm$^{-1}$) are also noticed in the spectrum, which means the protein secondary structure, namely amides I and II [41]. It implies proteins as one of components of the biologic cell on the PDMS top surface. The FT-IR result provides another evidence of biological fouling.

We then used water to rinse the used PDMS membrane and evaluated its separation property in n-butanol/water. As depicted in Fig. 11, the separation property of fresh 40 cm-length PDMS/ceramic composite membrane were 683.6 g/m$^2$h for total flux and 28.6 for separation factor, respectively. After a simple water rinsing, the pervaporation...
performance was almost fully recovered, suggesting that the bio-fouling of membrane can be managed by intermittent water cleaning in practical applications.

3.4. Comparison with literature

Many methods have been applied for separation of fermentation products. Compared with other separation technologies coupled with fermentation, pervaporation is a green technology for its good selectivity, ease of operation, low energy consumption and no adverse effects on microorganism. A summary of butanol recovery property of PDMS composite membranes reported in the coupled process is listed in Table 2. Compared with PDMS membranes using polymeric substrate, the ceramic-supported PDMS composite membranes presents high total flux and separation factor of butanol/water. This is owing to the low transportation resistance of the macroporous ceramic substrate (average pore size: 200 nm) and the integrated PDMS thin layer. The property of PDMS composite membrane can even compete with that of the silicalite-1 incorporated PDMS mixed-matrix membrane, showing only a slightly lower separation factor due to the absence of the highly hydrophobic filler. Nevertheless, the pure polymeric membranes still dominate in practical implementation of membrane technology because of its easier fabrication and lower cost.

It is also interesting to compare the performance of PDMS composite membrane coated on inner and outer surface of ceramic tube. The inner surface coated PDMS membrane showed slightly lower (21%) averaged

<table>
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<tr>
<th>Membrane type</th>
<th>Feedstock</th>
<th>Temperature (°C)</th>
<th>Averaged total flux (g/m² h)</th>
<th>Averaged butanol/water separation factor</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS/ceramic (coated on outer surface)</td>
<td>Glucose</td>
<td>37</td>
<td>670</td>
<td>15.1</td>
<td>[29]</td>
</tr>
<tr>
<td>PDMS/PVDF</td>
<td>Glucose</td>
<td>37</td>
<td>310</td>
<td>22</td>
<td>[42]</td>
</tr>
<tr>
<td>PDMS/polyimide</td>
<td>Glucose</td>
<td>35</td>
<td>367</td>
<td>14.7</td>
<td>[43]</td>
</tr>
<tr>
<td>silicalite-1 filled PDMS</td>
<td>Glucose</td>
<td>37</td>
<td>448</td>
<td>31.6</td>
<td>[28]</td>
</tr>
<tr>
<td>silicalite-1 filled PDMS</td>
<td>Cassava</td>
<td>37</td>
<td>557</td>
<td>31</td>
<td>[44]</td>
</tr>
<tr>
<td>PDMS/ceramic (coated on inner surface)</td>
<td>Glycerol</td>
<td>37</td>
<td>509</td>
<td>24.7</td>
<td>This work</td>
</tr>
</tbody>
</table>

Fig. 12. (a–b) Separation property of PDMS composite membranes in the coupled process. PDMS membranes are coated on the (c) inner and (d) outer surface of ceramic tube, respectively. (b) Reproduced from Ref. [29]. Copyright Elsevier.
flux than that of the PDMS membrane coated on the outer surface of ceramic tube. The length of the tubular ceramic support for the inner and outer surface PDMS coating are 40 and 14 cm respectively. As compared in Fig. 12a–b, the lower averaged flux can be simply attributed to the lower initial flux of the PDMS membrane (571 g/m² h for inner surface coating vs 650–750 g/m² h for outer surface coating). As mentioned above, the lower initial flux in the inner surface PDMS composite membrane is due to the thicker separation layer as coating the longer ceramic tube (40 cm). During the fermentation-pervaporation coupled process, we can also find a relatively stable separation factor in the inner surface PDMS composite membrane whereas a significantly declined separation factor for the outer surface PDMS composite membrane from 50 to 58 h (Fig. 12a–b). Thus, with a similar initial separation factor for both composite membranes, the inner surface coated PDMS membrane showed much higher (65%) averaged separation factor than that of the PDMS coated on the outer surface of ceramic tube. The difference in fermentation process should be also noted. Glycerol fermentation and glucose fermentation were applied for Fig. 12a and b, respectively. Nevertheless, the initial separation factor of the PDMS membranes in the two fermentation processes is similar. The variation of separation factor can be mainly ascribed to the different flow distributions in the inner and outer surface PDMS composite membrane.

Fig. 12c shows a typical cross-flow operation of pervaporation separation using tubular membrane. In accordance with the separation layer (PDMS) on the inner and outer surface of the ceramic tube, the fermentation broth is fed into the bore side and shell side, respectively. In the outer membrane module (Fig. 12d), there are two dead end regions in the both ends of the module, due to the influence of the feed inlet and outlet position and feed flow rate [45–48]. The occurrence of stagnant zone and concentration polarization cause bacteria growth on the surface of membrane and eventually result in the reduction of membrane property. In contrast, the feed flow distribution in inner surface module is uniform along the membrane tube (Fig. 12c), which is conductive to reduce the bacterial growth and membrane fouling and thus favor of preserving a stable separation factor [17,49,50].

4. Conclusions
In this work, inner surface of ceramic tube supported PDMS pervaporation membrane was employed for in-situ butanol removal from glycerol fermentation. It was discovered that the PDMS/ceramic composite membrane presented highly selective permeation for products (butanol and ethanol), whereas non-selective for intermediates (acetic acid and butyrate acid) and rejection for substrate (glycerol) and inorganic salts. Integrating the PDMS membrane increased the butanol yield by 33% and productivity by 89% of the alone glycerol fermentation in a continuous and closed-circulating fermentation system with PDMS membrane bioreactor, Bioreour. Technol. 128 (2013) 246–251.

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